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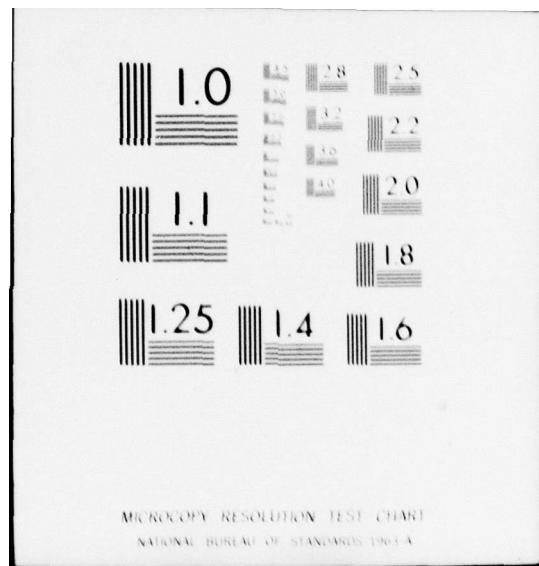
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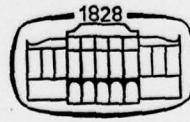
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FOURTH SYMPOSIUM ON RADIATION CHEMISTRY, 1976

MATRIX ENDOR STUDIES OF THE ORIENTATION OF AMINE MOLECULES
AROUND TRAPPED ELECTRONS IN γ -IRRADIATED AMINE GLASSES

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Introduction

Solvated electrons produced in organic systems by ionizing radiation have excited considerable theoretical and experimental interest /1/. The kinetic features of electron solvation studied by pulse radiolysis, particularly in alcohols /2, 3/, and the geometrical features studied by pulsed and double electron magnetic resonance techniques in alkanes /4/, ethers /5-7/, alcohols /5, 6, 8/ and even aqueous systems /9-11/ are beginning to emerge. The geometrical features are best studied in glassy matrices in which the electrons can be stabilized for relatively long times. Electrons are also solvated in glassy aliphatic amines /12-17/ but little structural information has yet been deduced for such systems. In primary and secondary amines it is easy to replace the NH protons by deuterons so that electron paramagnetic resonance (EPR) and electron nuclear double resonance (ENDOR) linewidth studies should yield structural data.

In EPR studies at 77K, the EPR linewidths of trapped solvated electrons are reported to be 24-25G for primary amines, 6.5-14G for secondary amines and 3-4G for tertiary amines /12, 15, 16/. The optical absorption spectra of these trapped, solvated electrons show small but noticeable spectral differences particularly in the maximum absorption wavelength, λ_{max} , for the three types of amines /12-14/. These spectral differences have been generally interpreted as due to differences in molecular dipole moment and molecular structure of the amines. The dipole moments of aliphatic amines decrease from primary to secondary to tertiary. However, no specific structural differences have been deduced.

In this study we have chosen sec-butylamine (SBA), diisopropylamine (DIPA), and triethylamine (TEA) as representative primary, secondary, and tertiary amines, respectively. One objective is to deduce information about the molecular orientation of the various amines with respect to the electron by using partially deuterated amines. A second objective is to consider whether different size solvation shells account for the spectral differences between the primary, secondary and tertiary amines.

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Experimental

Amines bought from J. T. Baker Co. were purified as follows. The amine was first refluxed over potassium hydroxide pellets and then was repeatedly distilled under a nitrogen atmosphere. A middle portion of the distilled amine was collected, degassed, and treated with sodium-potassium alloy. The treated amine was stored in a bulb containing a freshly prepared potassium mirror to eliminate water remaining in the amine.

Partially deuterated amines, sec-butylamine-d₂ (SBA-d₂) and diisopropylamine-d₁ (DIPA-d) (with the NH protons replaced by deuterium), were prepared by repeatedly reacting the purified amine with D₂O (Stohler Isotope Co.). The percentage of deuteration can be adjusted by varying the volume percent of normal amine and D₂O. The final deuteration percentage was measured by mass spectrometry and nuclear magnetic resonance (NMR) spectroscopy.

The amine samples were sealed under vacuum in 7 mm I. D. spectrosil quartz tubing and quick frozen in liquid nitrogen to form glassy matrices. The samples were transferred at 77K to a ⁶⁰Co γ -source and irradiated in liquid nitrogen at dose rate of 0.22 Mrad/hr. The primary, secondary, and tertiary amines were given total doses of 4.8 Mrad, 3.1 Mrad and 2.0 Mrad, respectively, these doses correspond to the maximum yield of trapped electrons in these amines /7/. After irradiation, EPR and ENDOR measurements were immediately carried out in the dark to avoid electron decay and accidental photobleaching. The temperature during measurement was controlled by passing cold helium gas through a flow dewar in the ENDOR cavity.

EPR and ENDOR spectra were recorded with a Varian 4502 EPR spectrometer interfaced with a Varian E-700 ENDOR unit. ENDOR measurements were taken at a microwave power near the maximum intensity of the EPR microwave saturation curve of the trapped electron. The rf magnetic field was set near its maximum value of 5-6G.

Results

Primary amine:

In γ -irradiated sec-butylamine (SBA), we observe two distinct EPR signals, depending on the microwave power applied. The linewidths of these two signals are not changed when normal SBA is replaced by SBA-d₂. Figure 1 shows the first derivative of the EPR spectra at 0.7 and 8 mW microwave power and 36K obtained from SBA-d₂. Using a microwave power $H_1 = 8\text{mM}$, we observe a there line pattern from which, by means of photobleaching and spectral subtraction, a broad singlet with a linewidth $\Delta H_{pp} \approx 23\text{G}$ could be obtained. This singlet, referred to here as signal A, has been reported and interpreted as due to a trapped electron in this amine /12, 17/. The main support for this interpretation appears to be that signal A can be bleached upon exposure to visible light. However, we have noticed that this EPR line has at least two peculiar features: (1) it has a similar microwave saturation curve to that of the

main three lines pattern with which it overlaps. (2) compared to other EPR signals of trapped electrons (for example to signal B of this amine and to those in DIPA and TEA), it is relatively stable to visible light.

On the other hand, when we reduce the microwave power by approximately one order of magnitude ($H_1 = 0.7$ mW), we observe that a much narrower singlet emerges from the broad background. This signal, referred to here as signal B, has a linewidth of $\Delta H_{pp} \approx 7$ G. To our knowledge this signal B has not been reported before. In addition to the dramatic difference in EPR linewidth compared to signal A, signal B is much more easily saturated by microwave power and more readily bleached by visible light.

ENDOR of both signals A and B has been attempted, however, only signal A ($\Delta H_{pp} \approx 23$ G) gave a response. The failure to obtain an ENDOR response from signal B ($\Delta H_{pp} \approx 7$ G) is probably due to the fact that the EPR signal is too weak. We have unsuccessfully tried to improve the conditions for ENDOR by using a partially deuterated sample (SBA-d₂) and also by varying the observation temperature. The matrix ENDOR line of signal A is shown in Fig. 2. The ENDOR linewidth (Δv) is 1.63 MHz in both SBA and SBA-d₂. Note that the signal-to-noise ratio of the ENDOR line is comparatively poor and that there is a slight contribution from the background radical (s). The radical contribution becomes more significant when the measurement temperature is lowered. However, the ENDOR line shown in Fig. 2 is mainly due to the bleachable component in the EPR spectrum.

Secondary Amine:

For a secondary amine, we have used undeuterated DIPA, 60% deuterated DIPA (60% of the NH protons being replaced by deuterons, DIPA-60% d) and 100% deuterated DIPA (100% of the NH protons being replaced by deuterons, DIPA-100% d). The percentage of deuteration was confirmed by NMR and mass spectroscopic measurements. The EPR spectrum of trapped electrons in γ -irradiated DIPA shows a singlet of linewidth $\Delta H_{pp} = 7.6$ G which, within experimental error, does not change when NH protons are replaced by deuterons. Figure 3 shows the ENDOR spectra of the trapped electrons in DIPA and DIPA-100% d. The microwave power applied to obtain the ENDOR response did not saturate the background radical (s). As indicated by photobleaching, these ENDOR lines do not have a radical contribution. As shown in Table 1, the ENDOR linewidths in undeuterated and partially deuterated samples are essentially the same although the deuterated samples were reproducibly smaller when a relative comparison was made. Another interesting feature associated with the ENDOR spectra in DIPA is the existence of a pair of satellite ENDOR lines. These lines are better resolved in partially deuterated samples, as can be seen in Fig. 3. The distance between the satellite line at the high frequency side to the center of the matrix line is approximately 2 MHz. The intensity of the corresponding satellite at the low frequency side is smaller, a phenomenon generally observed for ENDOR spectra. A similar situation has been recently reported in the ethylene glycol/water matrix irradiated and measured at 4.2K [6].

Tertiary Amine:

The EPR spectrum associated with the trapped electron in γ -irradiated triethylamine (TEA) is a very narrow singlet of linewidth $\Delta H_{pp} = 4G$, as reported by other workers /12, 15-17/. As in the case of DIPA, the saturation curve of this trapped electron by microwave power is distinctly different from that of the background rad-

Table 1
EPR and ENDOR linewidths of trapped electrons produced in γ -irradiated normal and partially deuterated diisopropylamines at 70K

Sample	EPR Linewidth	ENDOR Linewidth ^a	Measurement Temperature
DIPA	7. 6 G	1. 58 MHz	70K
DIPA-60% d	7. 6 G	1. 54 MHz	70K
DIPA-100% d	7. 6 G	1. 54 MHz	70K

^a Estimated error is ± 0.02 MHz

Table 2
EPR and ENDOR linewidths of trapped electrons produced in γ -irradiated primary, secondary, and tertiary amine glasses at 77K

Amine	EPR Linewidths	ENDOR Linewidths ^a	ENDOR Satellite	Background radical contribution to ENDOR ^b	Measurement temperature
Signal B of SBA	7. 0 G	No ENDOR	-	-	68-72 K
Signal A of SBA	23-24 G	1. 63 MHz	No	Small	68-72 K
DIPA	7. 6 G	1. 58 MHz	Yes	None	67-70 K
TEA	4. 0 G	1. 89 MHz	No	None	40-70 K

^a Estimated error is ± 0.02 MHz.

^b Determined from ENDOR response at the same magnetic field after the sample was exposed to visible light.

ical (s). The EPR and ENDOR spectra of this trapped electron in TEA are shown in Fig. 4. Unlike that in DIPA, the ENDOR spectrum in TEA shows no satellite ENDOR lines. The matrix ENDOR linewidth ($\Delta\nu = 1.89$ MHz) in TEA is considerably larger than that in DIPA ($\Delta\nu = 1.58$ MHz). The EPR and ENDOR linewidths of the three amines are summarized in Table 2.

Discussion

The ENDOR responses observed in the present systems can be divided into two groups: the matrix ENDOR lines and the satellite ENDOR lines. The matrix ENDOR line which occurs at the free proton resonance frequency, can be interpreted as resulting primarily from dipolar interaction between the unpaired electron and the protons of the surrounding amine molecules /5, 18/, any contact interaction associated with these protons would shift the line away from the free proton frequency. The ENDOR linewidth decreases as the average distance to the dipolarly coupled protons increases, so if some of these protons are replaced by deuterons, the linewidth of the matrix ENDOR lines will be reduced. The satellite ENDOR lines, on the other hand, indicate some isotropic hyperfine interaction between the unpaired electron and its nearby protons. Such satellite ENDOR lines occur in pairs centered about the free proton frequency. However, the low frequency satellite ENDOR line is typically much weaker than the high frequency one.

Primary Amine:

In sec-butylamine, there appear to be two distinct EPR singlets: signal A and signal B. The interpretation that signal A is due to a trapped electron seems questionable for the reasons described in the results section. Furthermore, the rather broad EPR linewidth ($\Delta H_{pp} = 23$ G) does not seem compatible with all other trapped electrons observed. Therefore, we suggest this signal is a radical species which is unstable to visible light. It is also possible that signal A is due to a trapped electron which is strongly coupled to nitrogen nuclei which broaden its EPR line and shorten its relaxation time. The EPR and ENDOR data obtained here are not sufficient to distinguish these possibilities; ^{15}N substitution is needed.

It is significant that we observe signal B at lower microwave power than for signal A. This is typical of trapped electron signals, so we assign this signal to a trapped electron. Other reasons that support this assignment are the following: (1) Signal B has a g-value close to the free spin value; (2) Signal B is very sensitive to visible light and has a saturation curve very different from that of the background radical (s); (3) The linewidth $\Delta H_{pp} = 7$ G seems compatible with that for other trapped electrons in slightly polar systems. The weakness of signal B implies a relatively low concentration of trapped electrons, and suggests that SBA is an inefficient matrix for trapping electrons. This low trapping efficiency is perhaps not surprising in view of the low symmetry of the SBA molecule.

The identity of the EPR linewidth of signal B in both SBA and SBA-d₂ indicates that the spin of the electron has negligible contact interaction with the NH protons of the amine molecules. This appears to imply that the orientation of the amine molecules in the first solvation shell is such that the CH protons are closer to the trapped electron than are the NH protons.

Secondary amine:

There also appears to be no deuteration effect on the EPR linewidth for the trapped electron in di-isopropylamine, although there may possibly be a small effect on the matrix ENDOR linewidth. This indicates that there is nearly negligible hyperfine interaction involving the NH protons. The presence of a proton ENDOR satellite line and its enhancement in deuterated samples (DIPA - 100% d) imply that there is contact interaction between the unpaired electron and the CH protons, but not the NH protons.

In both SBA and DIPA we conclude that the electron does not interact significantly with the NH protons. Thus the electron is essentially in an alkane environment. A probable model for electron solvation is that the electron interacts with a methyl group from each of several amine molecules, in its first solvation shell. Interaction with CH and CH₂ protons is also possible but seems less probable due to steric factors. From electron spin echo modulation studies on ethers /7/ and alkanes /19/, it seems likely that there are 4-6 amine molecules in the first solvation shell. The similarity of the EPR linewidths in SBA and DIPA suggests that the distance from the electron to the first solvation shell protons is similar. Furthermore, the contact interaction inferred from the ENDOR data on DIPA suggests that the electron wavefunction is quite delocalized.

Tertiary Amine:

The linewidth ($\Delta H_{pp} = 4.0$ G) of the EPR line associated with the trapped electron in triethylamine is the narrowest among the three types of amines studied here. Note that this linewidth is very comparable to those observed for trapped electrons in alkane systems /1/. The similarity seems to indicate that in TEA the trapped electron is surrounded by alkyl protons with about the same geometry as for trapped electrons in alkane glasses. The absence of satellite ENDOR lines means that there is negligible contact interaction between the trapped electron and the closest alkyl protons. This is consistent with the larger EPR linewidth observed in SBA and DIPA.

As pointed out at the beginning of the discussion the matrix ENDOR linewidth decreases as the average distance to the dipolarly coupled proton increases. Since the matrix ENDOR linewidth in DIPA (1.58 MHz) is less than in TEA (1.89 MHz), this says that the dipolarly coupled protons are further away in DIPA. A quantitative

analysis assuming a nuclear spin packet linewidth of 100 Hz leads to a relation between the full width at half-height of the ENDOR line and the distance to purely dipolarly coupled protons/5/. Application to the data for DIPA and TEA gives a 0.2 Å distance difference. However, this does not mean that the trapped electron cavity in DIPA is larger than in TEA, because in DIPA the closest matrix protons to the electron have some contact hyperfine coupling and do not contribute to the matrix ENDOR line. The next nearest protons in DIPA, which we assume are purely dipolarly coupled to the electron, are ~0.2 Å further away from the electron than the nearest protons in TEA.

The ENDOR results on TEA suggest that the 4 G EPR linewidth is due to purely dipolarly coupled protons. Then we can use Eq. (1) /4/ to calculate an average distance to the closest n equivalent protons. We assume $n = 12$ to 18

$$r(\text{\AA}) = (40 n^{1/2} / A_{\text{pp}})^{1/3} \quad (1)$$

based on an analysis of electron spin echo modulation results /19/. These n values correspond to about 4-6 first solvation shell molecules interacting with the electron. The results are $r = 3.3 \text{\AA}$ for $n = 12$ and $r = 3.5 \text{\AA}$ for $n = 18$.

Summary

The NH deuteration experiments indicate that the alkyl protons of primary and secondary amines are closer than the NH protons to the trapped electron. The larger trapped electron EPR linewidths in primary and secondary amines compared to tertiary amines suggests a small contact hyperfine proton coupling, this is supported by the ENDOR data. The ENDOR and EPR results on trapped electrons in tertiary amines suggest that the proton interaction is purely dipolar and that the closest protons are ~3.4 Å from the electron. In the more polar primary and secondary amines the small proton contact interaction suggests that the closest protons are < 3.4 Å from the electron.

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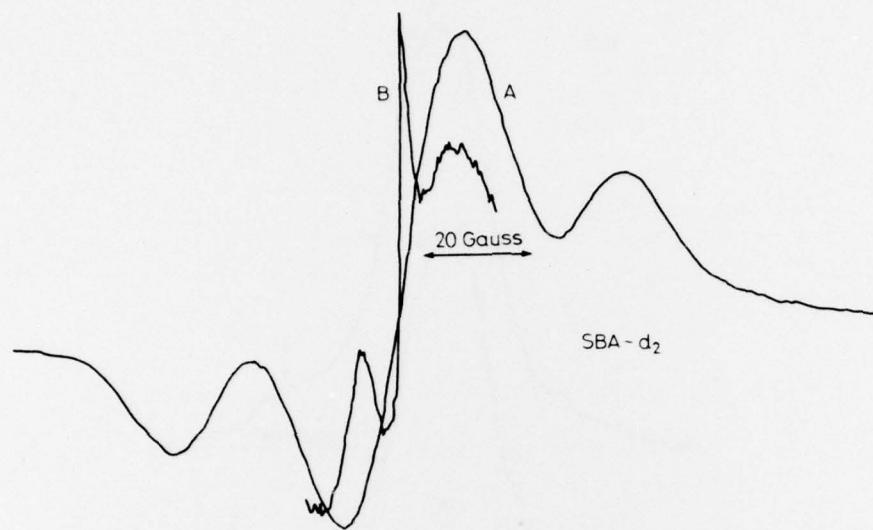


Fig. 1. EPR spectra obtained from γ -irradiated dideutero sec-butylamine at 36 ± 2 K showing two different signals, depending on the microwave power applied. Signal A is taken with $P = 8$ mW, $H_m = 2$ G and signal B with $P = 0.7$ mW, $H_m = 0.2$ G

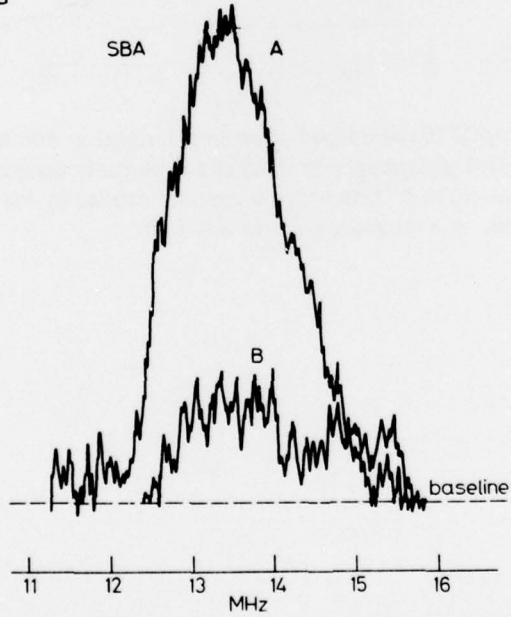


Fig. 2. Matrix ENDOR of EPR signal A of γ -irradiated sec-butylamine at 68 K before (A) and after (B) photobleaching with visible light

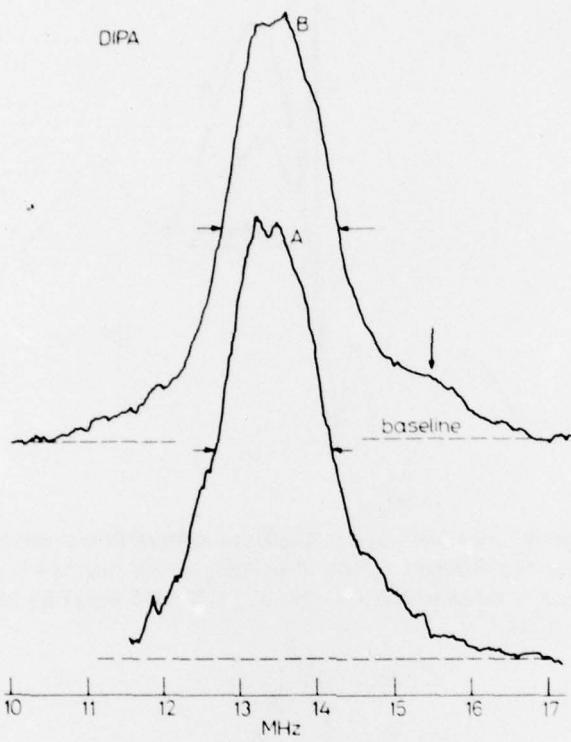


Fig. 3. Matrix ENDOR of the trapped electron EPR signal at 68K in γ -irradiated undeuterated disopropylamine (A) and in partially deuterated diisopropylamine DIPA-100% d (B) in which a shoulder marked by the arrow is clearly observable. The microwave power is 3.5 mW

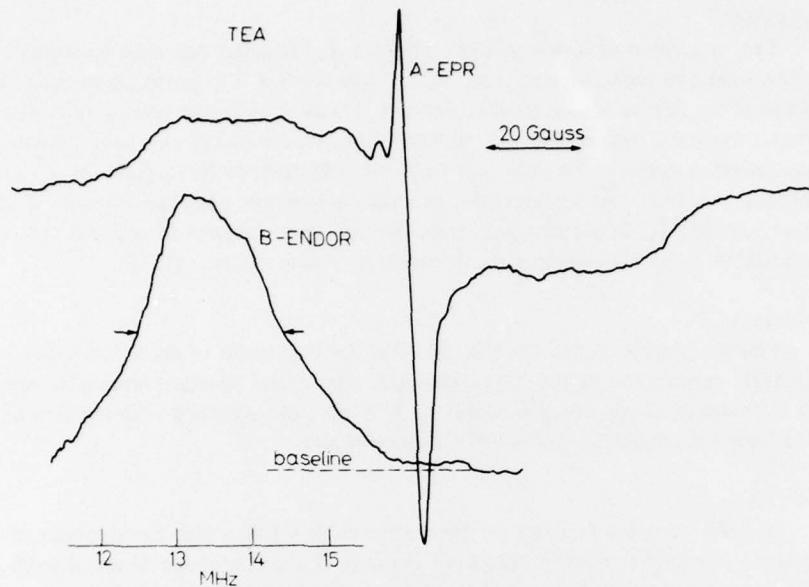


Fig. 4. Spectrum A shows the EPR of γ -irradiated triethylamine at 68K. Spectrum B shows the trapped electron while observing the EPR at the minimum of the derivative curve at 3.5 mW microwave power

DISCUSSION

Yu. D. TSVETKOV

Have you any idea about the arrangement of the second solvation shell of trapped electron in amine glasses?

L. KEVAN

No. To do this we need an experimental technique that is sensitive to much larger distances ($\gtrsim 10 \text{ \AA}$) than we have now.

Yu. A. BERLIN

Is it correct to say that the value of radius between e_{tr}^- and H you have found may be attributed to the size of traps for the localized electron? Can you compare this value with data obtained by other authors?

L. KEVAN

Yes, our value of 3.4 \AA in TEA defines a trap size but you must be careful to define what you mean by trap size. In our case the 3.4 \AA corresponds to the nearest proton of the first solvation shell molecules. No other data has been obtained of which I know for trapped electron in TEA. However, we have obtained distance data for other systems. For electrons in 2-methyltetrahydrofuran glass the e^- -H distance is $3.1\text{--}3.2 \text{ \AA}$. For electrons in 3-methylpentane glass the distance is also about $3.1\text{--}3.2 \text{ \AA}$. These distances were derived from analyses of electron spin echo modulation data. For example see L. Kevan, J. Chem. Phys., (1975).

J. SOHMA

You mentioned that in the case of DIPA the line width of the ENDOR spectrum is mainly determined by the interaction with the second nearest protons, in spite of the appearance of the isotropic coupling. Why does the coupling with the first nearest neighbour not contribute to the ENDOR line-width?

L. KEVAN

In DIPA we see a shoulder on the matrix ENDOR line which we attribute to isotropic coupling to nearest neighbour protons. If the line shape of this shoulder is estimated and this is subtracted from the matrix ENDOR line we will have a residual matrix ENDOR line that will be narrower than we reported. This corrected matrix ENDOR line will be mainly due to the next nearest neighbour protons. Protons which have much of an isotropic coupling, in this case the nearest neighbour protons, are split out from the free proton transport frequency and contribute little to the matrix ENDOR line.

I should mention that the semiquantitative relation of the matrix ENDOR line-width and the minimum dipolar coupling distance is based on a very simple model which should be improved. We are currently trying to develop such an improved model which incorporates all dipolar interaction, forbidden spin transitions and dependencies on microwave and radio frequency magnetic field magnitudes.

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contact hyperfine coupling; this is supported by ENDOR data. In tertiary amines EPR and ENDOR results on trapped electrons suggest that the proton interaction is purely dipolar and that the closest protons are $< 3.4 \text{ \AA}$ from the electron. In the more polar primary and secondary amines the small proton contact interaction suggests that the closest protons are $< 3.4 \text{ \AA}$ from the electron.

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